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- (54) **Process for producing and use of maleic acid (co-) polymer salt improved in biodegradability.**

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## Description

## BACKGROUND OF THE INVENTION

5 The present invention relates to a process for producing and use of maleic acid (co-)polymer salt improved in biodegradability. In detail, it relates to a process for producing a maleic acid (co-)polymer salt improved in biodegradability, which is very useful as a detergent builder, a scale inhibitor, and various kinds of chelating agents etc., by using a specially defined polymerization catalyzer and a specially defined polymerization method, with high efficiency and cheap cost, and also, relates to the use as a detergent  
 10 builder and a scale inhibitor etc.

As a detergent builder, a scale inhibitor, and a chelating agent etc., an additive in a phosphorus series such as a condensed phosphoric acid salt and a phosphonic acid salt has so far been used. However, when run into the sea or lake through a river etc., these become an original substance for a red tide etc., so that their use is very limited. Thus, instead of the additive in the phosphorus series, an additive in a series of  
 15 polycarboxylic acid salts has practically been used in recent years in the forementioned field and in large quantity. However, the additive in a series of polycarboxylic acid salts so far been used are all poor in the biodegradability and, for example, in a case of that it is used in large quantity as a detergent builder or a scale inhibitor etc., there may take place such a greatly serious problem as the accumulation in circumstances.

For example, although there is proposed a maleic acid (co-)polymer (salt), which is obtained with polymerization in a mixture solvent of water and a primary alcohol of carbon number 1~ 4 or a ketone of carbon number 3 ~ 4 in Japanese Official Patent Provisional Publication, showa 62-91295, and Japanese Official Patent Provisional Publication, showa 62-91296, the maleic acid (co-)polymer (salt) disclosed in these literatures was low in biodegradability and insufficient in properties as a scale inhibitor. Besides, in  
 20 these arts, a maleic acid (co-) polymer (salt) of high polymerization percentage was not obtained. Also, although there are proposed maleic acid (co-)polymer salts obtained by a polymerization in water solvent under presence of hydrogen peroxide, which were described in Japanese Official Patent Provisional Publications, showa 57-168906 (USP4,519,920), showa 59-64615 (USP4,668,735), showa 59-176312 (USP4,589,995), showa 59-210913, showa 59-213714, showa 60-212410, showa 60-212411 (USP4,709,091),  
 25 showa 60-212412, showa 61-178097, showa 62-218407 (USP4,659,793) showa 63,114986, showa 63-235313, and showa 63-236600, the maleic acid (co-) polymer salts disclosed in these literatures show very inferior biodegradability. There is no description about the biodegradability in all said literatures.

EP-A-0,337,694 discloses a process for producing an acid-type maleic acid polymer by polymerizing, in an aqueous solution, a monomer component composed of maleic acid alone or a monomer component  
 35 composed of 50-99.9 weight % of maleic acid and 50-0.1 weight % of another water-soluble unsaturated monomer, in the presence of at least one metal ion selected from an iron ion, a vanadium atom-containing ion, and a copper ion by the aid of hydrogen peroxide as the polymer catalyst. However, the polymer obtainable by this process does not exhibit very high biodegradability, because the neutralization degree of this polymer is 0%. Furthermore, comparative examples of the EP-A-0,337,694 disclose addition of an  
 40 alkaline substance during the polymerization reactions. However, maleic acid polymers obtainable from the comparative examples exhibit poor biodegradability, because the neutralization degree of the polymers is 50% or more, which is too high, or because a polymerization medium other than water is used together with water.

EP-A-0,236,103 discloses a process for producing a water-soluble copolymer by copolymerizing a  
 45 monoethylenically unsaturated dicarboxylic acid monomer and an  $\alpha,\beta$ -ethylenically unsaturated monomer in an aqueous solution system in the presence of a metal ion selected from  $Zn^{2+}$ ,  $Co^{3+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Mo^{2+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$ ,  $Ce^{4+}$  and  $Ce^{2+}$  while maintaining the pH of the aqueous solution system at 2-7 to reduce the residual content of unpolymerized dicarboxylic acid. However, the copolymer obtainable by this process exhibits poor biodegradability because the content of the dicarboxylic acid such as maleic acid in  
 50 monomer components to be polymerized is 70 weight % or less, and because the amount of a polymerization initiator such as hydrogen peroxide is insufficient.

EP-A-0,346,964 discloses a process for producing a copolymer having a molecular weight of 50,000-150,000 by copolymerizing ethylenically unsaturated mono and dicarboxylic acids and water-insoluble aliphatic esters of ethylenically unsaturated monocarboxylic acids in an aqueous medium at a pH of 2.5-5.5.  
 55 However, in EP-A-0,346,964 there is no specific description of a polymer produced from a monomer component composed of 50 weight % or more of maleic acid and furthermore there is no description on the biodegradability of the polymers obtained according to EP-A-0,346,964.

On the other hand, although there is described in "YUKAGAKU, 35, 937 (1986)" that sodium poly- $\beta$ -DL-malic acid which is formed with ring-opening polymerization of malolactone shows high biodegradation percentage, properties of this polymer as a detergent builder is insufficient, and the synthesis of this polymer requires a complex process, so that the industrial utility is low. Also, there is described a polymer of  $\alpha$ -hydroxyacrylic acid which shows high biodegradability, but this polymer decomposes only with specially defined bacteria, and the synthesis of this polymer requires a complex process and, as a result, it becomes very expensive, so that the industrial utility is low.

Therefore, there has been greatly desired a process with which a polycarboxylic acid salt which has useful biodegradability as a detergent builder, a scale inhibitor, and various kinds of chelating agents etc is produced with cheap cost and in a high yield.

## SUMMARY OF THE INVENTION

As a result of extensive studies, the present inventors improved the low biodegradability of a polycarboxylic acid salt hitherto known. Furthermore, they greatly raised the industrial utility by improving the inadequate properties of a hitherto known polycarboxylic acid salt as a detergent builder and a scale inhibitor.

That is, the first present invention relates to a process for producing a maleic acid (co-)polymer salt improved in biodegradability which, in a case of that a monomer component composed of 75 ~ 100 weight % of maleic acid (A) and 25 ~ 0 weight % of the other water-soluble unsaturated monomer (B) (here, the total amount of (A) and (B) is 100 weight %) is polymerized in water as solvent is specialized by that 12~150 g of hydrogen peroxide (against 1 mole of the monomer component) is used as a polymerization catalyzer and the polymerization is carried out under a condition of that there exist 0.3 ~ 500 ppm (against weight of the monomer component) of at least a kind of polyvalent metal ion selected from an ion containing vanadium atom, an iron ion, and a copper ion as well as an alkaline substance which is required to neutralize 45 mole % or less of the whole acid group in the monomer component (but, except the 0 mole %).

The second and the third present invention, respectively, relate to the invention in use as a detergent builder and a scale inhibitor, both of which are specialized by being composed of a maleic acid (co-)polymer salt improved in biodegradability that is obtained from said process for producing in the first present invention.

In this invention, it is necessary to surely use water as a polymerization media. When a hydrophobic solvent alone such as an aromatic hydrocarbon, a hydrophilic solvent alone such as alcohol and ketone, and a mixture solvent such as a mixture of water with these hydrophilic solvents are used as a solvent in polymerization, the biodegradability is greatly lowered due to difference between a terminal end group or a main chain structure of a polymer and that of the maleic acid (co-)polymer salt in the present invention. That is, the biodegradability is lowered by because either the terminal end was an alcoholic or ketonic residue or because decarboxylation does not occur.

In the present invention, when the monomer component containing maleic acid is polymerized in an aqueous solution, it is essential that the polymerization is carried out under a condition of that there exist at least one kind of polyvalent metal ion selected from an ion containing a vanadium atom, an iron ion, and a copper ion in amount in a range of 0.3~ 500 ppm against the monomer component (standard weight of an acid form). Preferably, it is a range of 0.5 ~ 300 ppm and, more preferably, a range of 1 ~ 50 ppm. If the amount used is less than 0.3 ppm, a residual monomer increases unpreferably. If the amount for use exceeds 500 ppm, the biodegradability decreases. Furthermore, the product purity decreases unpreferably. Also, in a case where an ion other than an ion containing a vanadium atom, an iron ion, and a copper ion is used, the amount of the residual monomer increases as in a case where any metal ion is not used at all, and the biodegradability becomes low.

As an ion containing a vanadium atom, an iron ion, and a copper ion being used in this invention, for example, there are cited  $V^{2+}$ ,  $V^{3+}$ ,  $VO^{2+}$ ,  $VO_3^{2-}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ , and so on, but among those, are preferred  $VO^{2+}$ ,  $Fe^{3+}$ , and  $Cu^{2+}$ . In a case where elevation of polymerization yield is aimed, the  $VO^{2+}$  ion is most preferred. The polyvalent metal ion is not especially limited in the form being supplied in to a polymerization system, and if it is capable of ionizing in a polymerization system, it can be used as a polyvalent metal compound or as a simple substance.

As a polyvalent metal compound or a simple substance like the above, for example, are cited water-soluble polyvalent metal salts such as vanadium oxytrichloride, vanadium trichloride, vanadyl oxalate, vanadyl sulfate, anhydrous vanadic acid, ammonium methavanadic acid, ammonium hypovanadous sulfate  $((NH_4)_2SO_4 \cdot VSO_4 \cdot 6 H_2O)$ , ammonium vanadous sulfate  $((NH_4)VSO_4 \cdot 12 H_2O)$ , cupric acetate, cupric

bromide, cupric acetyl acetate, ammonium cupric chloride, cupric carbonate, cupric chloride, cupric citrate, cupric formate, cupric hydroxylic acid, cupric nitrate, cupric naphthenic acid, cupric oleinic acid, cupric maleic acid, cupric phosphate, cupric sulfate, iron acetyl acetate, ammonium iron citrate, ammonium ferric oxalate, ammonium ferrous sulfate, ammonium ferric sulfate, iron citrate, iron fumarate, iron maleate, 5 ferrous lactate, ferric nitrate, iron pentacarbonyl, ferric phosphate, ferric pyrophosphate and so on; polyvalent metal oxides such as vanadium pentaoxide, cupric oxide, ferrous oxide, ferric oxide, and so on; polyvalent metal sulfides such as cupric sulfide, ferric sulfide, iron sulfide, and so on; others such as copper powder, iron powder, and so on.

Furthermore, in order to adjust the ion concentration of the polyvalent metal ions, it is possible to use, 10 in combination with the forementioned polyvalent metal ions, for example, a chelate-forming agent in a series of condensed phosphoric acids such as pyrophosphoric acid, hexamethaphosphoric acid, and tripolyphosphoric acid etc.; in a series of aminocarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid, and diethylenetriaminepentaacetic acid etc.; in a series of phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid etc.; in a series of 15 organic acids such as fumaric acid, malic acid, citric acid, itaconic acid, oxalic acid, and crotonic acid etc.; and in a series of polycarboxylic acids such as polyacrylic acid etc. The polymerization temperature preferred is in a range of 85 ~ 160 °C, because it fits with a purpose of shortage of polymerization time and elevation of the biodegradability. The more preferable temperature is in a range of 100 ~ 150 °C. If the temperature is less than 85 °C, the polymerization process may be disturbed. During polymerization, a 20 solid portion is performable in a wide range, but the 30 ~ 99 weight %, more preferably the range of 40 ~ 95 weight % is recommended because of capability to decrease the amount of the residual monomer.

In the present invention, there is required 12 -150 g (against 1 mole of a monomer component) as an polymerization initiator. Preferably 15 ~ 100 g (against 1 mole of a monomer component) and more preferably 20 ~ 70 g (against 1 mole of a monomer component) is used. In a case where an amount less 25 than 12 g (against 1 mole of a monomer component), a maleic acid (co-)polymer salt which is superior in biodegradability cannot be obtained. In a case where an amount exceeding 150 g (against 1 mole of a monomer component), although the biodegradability does not decrease, hydrogen peroxide is apt to remain in the obtained maleic acid (co-) polymer salt and the cost for production increases, so that an amount of 150 g or less is used as very preferable. Also, if the hydrogen peroxide is replaced with another water- 30 soluble initiator, for example, with a persulfate salt such as ammonium persulfate, sodium persulfate, and potassium persulfate etc.; a hydrophilic organic peroxide such as tertiary-butyl hydroperoxide etc.; an water-soluble azo compound such as 2,2'-azobis(2-aminozinopropane) hydrochloric acid salt etc., a maleic acid (co-)polymer salt, which has superior biodegradability as that in this invention, cannot be obtained. A method to supply the hydrogen peroxide into water is not especially limited and, for example, it is carried 35 out by one time-pouring into the reaction system at a initial stage, continuous pouring into the reaction system, or in a case, dividing followed by pouring into the system.

In the present invention, the polymerization requires to be carried out under the condition that an alkaline substance necessary for neutralizing 45 mole % or less (but except for the 0 mole %) of the whole acid group of the monomer component exists. A preferable range can be set as 5 ~ 40 mole %. A maleic 40 acid (co-) polymer salt, which is obtained under the condition that an alkaline substance exceeding 45 mole % exists, shows inferior biodegradability.

As described above, if the existing amount of the alkaline substance exceeds 45 mole % against the whole acid group, or if an especially defined amount of an especially defined polyvalent metal ion or an amount of 12 g or more of hydrogen peroxide is not used, the obtained maleic acid (co-) polymer salt show 45 very inferior biodegradability.

Although there is no special limitation for the alkaline substance, suitable examples include the hydroxides or carbonates of alkali metals such as sodium, potassium, and lithium etc.; ammonia; the alkylamines such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, and triethylamine etc.; the alkanolamines such as monoethanolamine, diethanolamine, triethanolamine, 50 isopropanolamine, and dimethylethanolamine etc.; pyridine and so on. Among those, the hydroxides and carbonates of alkali metals, since they are of cheap cost and most easily available in an industrial viewpoint, are especially preferred.

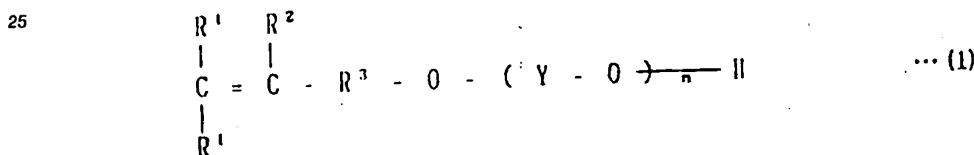
Also, the maleic acid (co-)polymer salt in this invention is required to be derived from a monomer component which contains 75 weight % or more of maleic acid (in a case of that the water-soluble 55 unsaturated monomer (B) is a monomer of a salt form, it is necessary that the amount for use is 25 % or less on a standard of the acid form). More preferably the amount can be 80 weight % or more. A maleic acid (co-)polymer salt, which is led from polymerization of a monomer component that contains less than 75 weight % of maleic acid, shows very inferior biodegradability.

It should be noted that the present invention should not be confused with a conventional art of component conditions similar to the present invention. For example, the maleic acid (co-)polymer salt, which is disclosed in said Japanese Official Patent Provisional Publication, showa 62-218407 (USP 4,659,793), show very inferior biodegradability because of any one of the undermentioned reasons, that is, because the amount of maleic acid used is less than that used in the case of the maleic acid (co-)polymer salt of the present invention, or because 12 g (against 1 mole of a monomer component) or more of hydrogen peroxide has not been used in an example of the publication, furthermore because the neutralization extent against the whole acid group is 50 % or more. Besides, there is no description about the biodegradation in the literature. The present invention subjugates a significant lack in the biodegradability of the maleic acid copolymer salt, which is opened in said Japanese Official Patent Provisional Publication, showa 62-218407 (USP 4,659,793), as well as insufficiency in properties which a detergent builder and a scale inhibitor etc. should have.

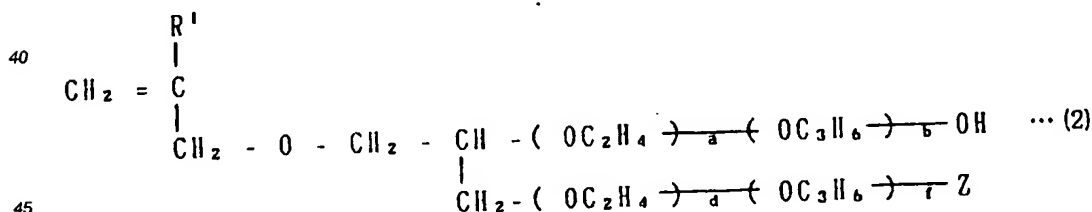
Besides, that maleic anhydride in replacement of maleic acid (A) can be used is of course, because the maleic anhydride easily reacts with water converting into maleic acid.

As far as the water-soluble unsaturated monomer (B) in this invention is water-soluble and a monomer capable of copolymerization with maleic acid, the monomer (B) can be used without any limitation. The polymer salts thus-derived from polymerization of maleic acid alone and from copolymerization with maleic acid show very high biodegradability compared with that of the conventional maleic acid (co-)polymer salt.

As the water-soluble unsaturated monomer (B), for example, are cited a monomer in a series of unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid,  $\alpha$ -hydroxyacrylic acid, and crotonic acid etc.; a monomer in a series of unsaturated polycarboxylic acids such as fumaric acid, itaconic acid, citraconic acid, and aconitic acid; a monomer which is shown by the general formula (1) in a series of unsaturated alcohols



(but in the formula, R<sup>1</sup> and R<sup>2</sup> independently represent a hydrogen atom or a methyl group and are not the methyl group at the same time, R<sup>3</sup> represents a -CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>2</sub>-, or -C(CH<sub>3</sub>)<sub>2</sub>- group and the total number of the carbon atom in the R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> groups in 3, Y represents a alkylene group of carbon number 2 ~ 3, and n is 0 or a integral number of 1 ~ 100) such as allyl alcohol and polyethyleneglycol monoallyl ether: a monomer which is shown by the general formula (2) in a series of unsaturated allyl ethers

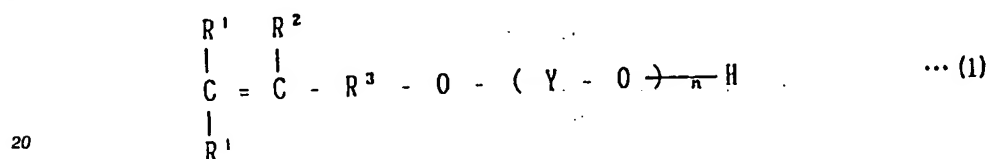


(but in the formula, R<sup>1</sup> represents a hydrogen atom or a methyl group, a, b, d, and f independently represent 0 or a positive integral number and the total number of a, b, d, and f is 0 ~ 10, the -(OC<sub>2</sub>H<sub>4</sub>)- and -(OC<sub>3</sub>H<sub>6</sub>)- units may be combined in any order, Z represents a hydroxyl, sulfonic acid, or phosphoric (or phosphorous) acid group when the sum of d and f is 0, and Z represents a hydroxyl group when the sum is a positive integral number of 1 ~ 100): a monomer containing a unsaturated sulfonic acid group such as vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, sulfoethylmaleimide, sulfopropyl (meth)acrylate, 2-hydroxysulfopropyl (meth)acrylate etc.: a monomer in a series of water-soluble mono- or diesters between an alcohol, which is formed with addition of 0 ~ 100 moles of ethylene oxide and/or propylene oxide to an alkylalcohol of carbon number 1 ~ 50, and (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, or aconitic acid etc.: a monomer in a series of mono- or di esters containing a water-soluble hydroxyl group which are

formed with addition of 1 ~ 100 moles of ethylene oxide and/or propylene oxide to a monomer in a series of unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, and aconitic acid etc.: a monomer in a series of unsaturated amides such as N-methylol(meth)acrylamide, (meth)acrylamide, tertiary-butyl (meth)acrylamide etc.: a monomer in a series of unsaturated phosphorus-containing compounds such as (meth)acrylamidomethanephosphonic acid, (meth)acrylamidomethanephosphonic acid methyl ester, and 2-(meth)acrylamido-2-methylpropanephosphonic acid etc.: and a monomer in a series of unsaturated aminoalkyl compounds such as dimethylaminoethyl (meth)acrylate and dimethylaminopropyl (meth)acrylamide etc., and one or two or more kinds of monomers selected from these groups can be used.

In a case where a maleic acid (co-)polymer salt obtained from a process for producing in the present invention is used as a detergent builder and a scale inhibitor, although there is no special limitation, the undermentioned unsaturated monomer is preferred as a water-soluble unsaturated monomer (B). That is, there are cited acrylic acid, methacrylic acid, a monomer in a series of unsaturated alcohol which is represented by the general formula (1),

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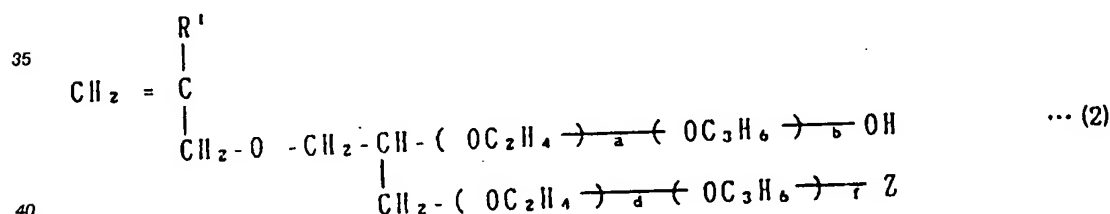


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(but in the formula, R<sup>1</sup> and R<sup>2</sup> independently represent a hydrogen atom or a methyl group and are not the methyl group at the same time, R<sup>3</sup> represents a -CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>2</sub>-, or -C(CH<sub>3</sub>)<sub>2</sub>- group, the total of carbon number in the R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> groups is 3, Y represents an alkylene group of carbon number 2~3, and n is 0 or a integral number of 1 ~ 100.),

for example, 3-methyl-3-buten-1-ol (isoprenol), 3-methyl-2-buten-1-ol (prenol), 2-methyl-3-buten-2-ol (isoprenealcohol) and a monomer which is formed with addition of 1~100 moles of ethylene oxide and/or propylene oxide to 1 mole of the forementioned unsaturated alcohol monomers (among them, isoprenol and polyethyleneglycol monoisoprenol ether are especially preferred.):

and a monomer in a series of unsaturated allyl ethers, which is shown by the general formula (2),



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(but in the formula, R<sup>1</sup> represents a hydrogen atom or a methyl group, a, b, d, and f independently represent 0 or a positive integral number and the total of a, b, d, and f is 0~100, the units -(OC<sub>2</sub>H<sub>4</sub>)- and -(OC<sub>3</sub>H<sub>6</sub>)- may be combined in any order, Z is a hydroxyl, sulfonic acid, or phosphoric (or phosphorous) acid group when the sum of d and f is 0, and Z is a hydroxyl group when the sum of d and f is a positive integral number of 1 ~ 100.),

for example, 3-(meth)allyloxy-2-hydroxypropanesulfonic acid, 3-(meth)allyloxy-2-hydroxypropanephosphorous acid, glycerol monoallyl ether, and a monomer which is formed with addition of 1 ~ 100 moles of ethylene oxide and/or propylene oxide to 1 mole of the forementioned allyl ether monomers (among them, 3-allyloxy-2-hydroxypropanesulfonic acid and glycerol monoallyl ether are especially preferred.) and the like. In the case where these monomers are used, the dispersion ability of a detergent against a dirty component and the protective property of a scale inhibitor for attaching and so on are elevated, very preferably as a detergent builder and a scale inhibitor.

Besides, although in this invention a monomer of a salt form, which is neutralized with an alkaline substance, is possible for use as the maleic acid (A) and water-soluble unsaturated monomer (B), in a case of that the monomer of a salt form is used, it is necessary to use an amount of that the neutralization extent for the whole acid group at the time of polymerization is 45 mole % or less (but except the 0 %).

Furthermore, a maleic acid (co-)polymer of an acid form which is obtained without use of an alkaline substance, and a maleic acid (co-)polymer salt which is obtained from neutralization of the above polymer with an alkaline substance, even if the neutralization extent is 45 mole % or less, shows low biodegradability.

5 According to the process for producing in this invention, a maleic acid (co-)polymer salt of 300 ~ 8,000 in molecular weight is usually obtained.

Why the maleic acid (co-)polymer salt obtained from the process described in this invention shows superior biodegradability is not yet clear, but it is guessed as follows. That is, decarbonylation takes place during polymerization and, as a result, a carbonyl group is formed in a main chain of the maleic acid (co-)polymer salt. Otherwise, an ether bond is formed in a main chain of the maleic acid (co-)polymer salt by 10 that a specially defined amount of a specially defined catalyzer for polymerization is used in a range of a specially defined neutralization extent and a specially defined polyvalent metal ion is used in a specially defined amount. Either one or both of the carbonyl structure and the ether bond is guessed to have a great effect on an increase of the biodegradability and an increase of properties as a detergent builder and a 15 scale inhibitor and the like.

Accordingly, in the process for producing in this invention, that the maleic acid (co-)polymer salt widely improved in biodegradability is obtained with high efficiency by that a definite amount in a range of hydrogen peroxide is used as a polymerization catalyzer under a condition of a specially defined neutralization extent and presence of a specially defined polyvalent metal ion, and that the (co-)polymer salt 20 has superior properties as a detergent builder and a scale inhibitor etc. can not predicted at all from the hitherto known conventional art.

The maleic acid (co-)polymer salt obtained from the process for producing in this invention shows no toxicity and much improved biodegradability compared with that of the hitherto known polycarboxylic acid salts and, for example, in a case of that it is used in large quantity as a detergent builder and a scale 25 inhibitor, an important problem such as accumulation in circumstances can be greatly improved and, therefore, it is of very high utility in an industrial viewpoint.

#### DESCRIPTION OF THE INVENTION

30 Hereinafter, although the present invention is concretely explained with the examples, it is not limited in the examples. Besides, the % and part in the examples indicate the weight % and weight part, respectively.

##### Example 1

35 Into a 1 l four-neck flask equipped with a thermometer, a stirrer, and a reflux condenser were placed 196 parts of maleic anhydride (232 parts as maleic acid), 75.1 part of deionized water, 0.0138 parts of vanadyl sulfate dihydrate (as  $\text{VO}^{2+}$ , 20 ppm against the weight of a monomer component), and 66.7 parts of a 48 % aqueous sodium hydroxide solution (20 mole % against the whole acid group of a monomer component) and, with stirring, the aqueous solution was brought to boiling temperature under ordinary 40 pressure. Next, 113.4 parts of 60 % hydrogen peroxide (34 g against 1 mole of a monomer component) was added dropwise continuously during 3 hours and a polymerization reaction was carried out. After the adding finished, the reaction mixture was stirred for further 1 hour at the boiling point of the mixture to complete the polymerization reaction, whereby a maleic acid polymer salt (1) of a 53 % solid component was obtained, which was analyzed by a gel permeation chromatography for determination of the amount of 45 the residual monomer and the molecular weight.

Besides, the biodegradation percentage (%) of a maleic acid polymer salt (1) obtained is determined with the following equation.

$$50 \quad X = \frac{A - B}{C - D} \times 100$$

- 55 X: Biodegradation percentage (%) during 5 days  
 A: Amount of oxygen biologically required by a maleic acid (co-)polymer (salt) during 5 days (BOD 5) (\*1)  
 B: Amount of oxygen biologically required by a residual monomer during 5 days (\*2)

C: Amount of oxygen theoretically required by a maleic acid (co-)polymer (salt) (\*3)  
 D: Amount of oxygen theoretically required by a residual monomer

(\*1) It was determined with the undermentioned method which is in turn due to the Japanese Industrial Standard; JIS K0102.

5 At first, to 1 l of distilled water, wherein the water temperature was adjusted to about 20 °C and dissolving oxygen was saturated, were added 1 ml of a buffer solution of pH 7.2 containing 21.75 g/l of dipotassium hydrogenphosphate (potassium hydrogen phosphate), 8.5 g/l of potassium dihydrogenphosphate, 44.6 g/l of disodium hydrogenphosphate 12-hydrate (sodium hydrogenphosphate 12-hydrate),  
 10 and 1.7 g/l of ammonium chloride, respectively, 1 ml of an aqueous magnesium sulfate solution containing 22.5 g/l of magnesium sulfate 7-hydrate, 1 ml of an aqueous calcium chloride solution containing 27.5 g/l of anhydrous calcium chloride, and 1 ml of an aqueous ferric chloride solution containing 0.25 g/l of ferric chloride 6-hydrate, whereby a diluted aqueous solution of pH 7.2 was prepared. Besides, this diluted aqueous solution was filled in the undermentioned bottle for cultivation and stood for 5 days in a thermostat of 20 °C, thereby it was confirmed that difference in the amounts of dissolved oxygen between the initial  
 15 time and after 5 days is 0.2 mgO/l or less.

Next, a diluted solution for inoculating was prepared by that a solution for inoculating composed of a supernatant fluid of a drain, a river water, a soil-extracting solution and the like was added to said diluted aqueous solution.

20 Next, using a siphon and giving attention to that a bubble does not enter in, said diluted aqueous solution or the diluted solution for inoculating was filled up to about a half of a 1 l messcylinder of a common stopper (in a case of that the undermentioned bottle for cultivation is 200 ml or more, a 2 l messcylinder of a common stopper is used). To this messcylinder was added a sample of proper amount and, to this, said diluted aqueous solution or the diluted solution for inoculating was added up to a 1 l symbol line (a 2 l symbol line in a case of that the messcylinder of a common stopper is 2 l), stopped,  
 25 and quietly mixed. Four or five kinds of diluted samples in which the dilution magnification differs stepwise were prepared by that a similar procedure was repeated with changing the amount of the sample or diluting a diluted sample again.

For each one kind of the diluted samples thus-prepared, respectively, 2 ~ 4 pieces of 100 ~ 300 ml bottles for cultivation, whose volumes are exactly known, made of a glass and equipped with a thin common  
 30 stopper, whose top is cut obliquely, were arranged and, using a siphon, said diluted samples were transferred into the bottles to fill with overflow and tightly stoppered.

Said diluted samples were stood for 15 minutes after being prepared, and an amount of dissolved oxygen was determined with a dissolved oxygen meter (D/O meter).

35 Said diluted samples were cultivated for 5 days in a thermostat or in a water bath of constant temperature whose temperature was adjusted at  $20 \pm 1$  °C and then, an amount of dissolved oxygen was determined as carried out above.

With the following equation, the BOD5 (mgO/l) was calculated of the sample from the dissolved oxygen amounts at before and after cultivation.

$$40 \quad BOD5 = \frac{(D_1 - D_2) - (B_1 - B_2) \times f}{P}$$

45 Here, BOD5 : an amount of oxygen consumed in a sense of biological chemistry when being cultivated for 5 days (mgO/l)

$D_1$  : an amount of oxygen dissolved in a diluted sample at 15 minutes later since it is prepared (mgO/l)

$D_2$  : an amount of oxygen dissolved in a diluted sample after cultivation (mgO/l)

50  $P$  : proportion of a sample in a diluted sample (a ratio of a sample to a diluted sample)

$B_1$  : an amount of oxygen dissolved in a diluted solution for inoculating before cultivation when BOD5 of the solution for inoculating is determined (mgO/l)

$B_2$  : an amount of oxygen dissolved in a diluted solution for inoculating after cultivation when BOD5 of the solution for inoculating is determined (mgO/l)

55  $f : \frac{x}{y}$

$x$  : a solution for inoculating in a diluted sample when BOD5 of a sample is determined (%)

$y$  : a solution for inoculating in a diluted solution for inoculating when BOD5 of a solution for inoculating is determined (%)



(\*2) The residual monomer amount is quantitatively analyzed with a gel permeation chromatography. The amount of oxygen in each monomer component biologically required is determined according to a method same to a case of the maleic acid (co-)polymer (salt) and the amount of oxygen in the whole residual monomer biologically required is obtained with calculation.

- 5 (\*3) The amount of oxygen necessary for complete oxidation was determined from the elementary analysis data of each maleic acid (co-)polymer (salt).

These results are shown in Table 1.

#### Example 2

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The procedure of example 1 was repeated to obtain the maleic acid polymer salt (2) except that the amount of 48 % aqueous sodium hydroxide solution in the example 1 was changed to 117 parts (35 mole % against the whole acid group of a monomer component). The maleic acid polymer salt (2) obtained was analyzed in the same way as carried out in the example 1, and the results obtained are shown in Table 1.

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#### Example 3

- 20 The procedure of example 1 was repeated to obtain the maleic acid polymer salt (3) except that the amount of 60 % hydrogen peroxide in the example 1 was changed to 50 parts (15 g against 1 mole of a monomer component) and 0.0412 parts of ammonium ferric sulfate 12-hydrate (as  $\text{Fe}^{3+}$ , 20 ppm against the weight of a monomer component) was used in place of vanadyl sulfate. The maleic acid polymer salt (3) obtained was analyzed in the same way as carried out in the example 1, and the results obtained are shown in Table 1.

#### 25 Examples 4 ~ 6

- 30 The procedure of example 1 was repeated to obtain the maleic acid polymer salts (4) ~ (6) except that ammonium ferric sulfate 12-hydrate was used in an amount shown in Table 1 instead of vanadyl sulfate and the amounts for use of a 48 % aqueous sodium hydroxide solution and the hydrogen peroxide were such as indicated in Table 1. The maleic acid polymer salts (4) ~ (6) were analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### Example 7

- 35 The procedure of example 1 was repeated to obtain the maleic acid polymer salt (7) except that 0.0335 parts of ammonium ferrous sulfate 6-hydrate (as  $\text{Fe}^{2+}$ , 20 ppm against the weight of a monomer component) was used instead of vanadyl sulfate. The maleic acid polymer salt (7) obtained was analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### 40 Example 8

- 45 The procedure of example 1 was repeated to obtain the maleic acid polymer salt (8) except that cupric sulfate was used in the amount shown in Table 1 instead of vanadyl sulfate and a 10 % aqueous sodium carbonate solution was used in the amount shown in Table 1 instead of the 48 % aqueous sodium hydroxide solution. The maleic acid polymer salt (8) obtained was analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### Example 9

- 50 In a vessel for polymerization as used in the example 1 were placed 232 parts of maleic acid, 39.1 parts of water, 0.0506 parts of ammonium ferric sulfate 12-hydrate (as  $\text{Fe}^{3+}$ , 20 ppm against the weight of a monomer component), and 66.7 parts of a 48 % aqueous sodium hydroxide solution (20 mole % against the whole acid group of a monomer component) and, with stirring, the aqueous solution was warmed up to the boiling point under ordinary pressure. Then, with stirring, a mixture of 151.6 parts of 60 % hydrogen peroxide (34 g against 1 mole of a monomer component) and, as the other water-soluble unsaturated monomer (B), 58 parts of 3-methyl-3-buten-1-ol (isoprenol) (a weight ratio between maleic acid and the water-soluble unsaturated monomer (B) was 80 to 20) was continuously added dropwise during 3 hours to carry out polymerization reaction. After the addition finished, the reaction mixture was further stirred for 1

hour at the boiling temperature to complete polymerization reaction, whereby the maleic acid copolymer salt (9) was obtained. The maleic acid copolymer salt (9) obtained was analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### 5 Examples 10 ~ 15

The procedure of example 9 was repeated to obtain the maleic acid copolymer salts (10)~ (15) except that the kind and amount for use of the polyvalent metal ion, the amount for use of the 48 % aqueous sodium hydroxide solution, and the amount for use of the 60 % hydrogen peroxide in the example 9 were as shown in Table 1. The maleic acid copolymer salts (10)~ (15) obtained were analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### Example 16

The procedure of example 9 was repeated to obtain the maleic acid copolymer salt (16) except that 153 parts of a 50 % aqueous sodium acrylate solution (as acrylic acid, 58 parts) was used instead of 3-methyl-3-buten-1-ol and the amounts for use of the 48 % aqueous sodium hydroxide solution and 60 % hydrogen peroxide were as shown in Table 1. The maleic acid copolymer salt (16) obtained was analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### 20 Examples 17 ~ 25

The procedure of example 9 was repeated to obtain the maleic acid copolymer salts (17)~ (25) except that the other water-soluble unsaturated monomers (B) as shown in Table 1 were used in the amounts described in Table 1 instead of 3-methyl-3-buten-1-ol and the kind and amount for use of the polyvalent metal ion and the amounts for use of the 48 % aqueous sodium hydroxide solution and 60 % hydrogen peroxide were as shown in Table 1. The maleic acid copolymer salts (17)~ (25) were analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### 30 Examples 26 ~ 28

The procedure of example 9 was repeated to obtain the maleic acid copolymer salts (26) ~ (28) except that the other water-soluble unsaturated monomers (B) as shown in Table 1 were used in the amounts described in Table 1 instead of 3-methyl-3-buten-1-ol and a 10 % aqueous sodium carbonate solution was used in an amount shown in Table 1 instead of the 48 % aqueous sodium hydroxide solution and the amount for use of 60 % hydrogen peroxide was as shown in Table 1. The maleic acid copolymer salts (26)~ (28) obtained were analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### 40 Example 29

In a vessel for polymerization same as used in the example 1 were placed 232 parts of maleic acid, 10 parts of water, 0.0412 parts of ammonium ferric sulfate 12-hydrate (as  $\text{Fe}^{3+}$ , 20 ppm against the weight of a monomer component), and 66.7 parts of a 48 % aqueous sodium hydroxide solution (20 mole % against the whole acid group of a monomer component) and then, the procedure of example 1 was repeated to obtain the maleic acid polymer salt (29). The maleic acid polymer salt (29) was analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

#### Examples 30 and 31

The procedure of example 9 was repeated to obtain the maleic acid copolymer salts (30) and (31) except that the other water soluble unsaturated monomers (B) as shown in Table 1 were used in the amounts shown in Table 1 instead of 3-methyl-3-buten-1-ol and the amounts for use of the 48 % aqueous sodium hydroxide solution and the 60 % hydrogen peroxide were as shown in Table 1. The maleic acid copolymer salts (30)~ (31) obtained were analyzed as carried out in the example 1, and the results obtained are shown in Table 1.

## Examples for comparison 1 ~ 3

The procedure of example 1 was repeated to obtain the maleic acid polymer salts for comparison (1) ~ (3) except that the kind and amount for use of the polyvalent metal ion, the amount for use of the 48 % aqueous sodium hydroxide solution, and the amount for use of the 60 % of hydrogen peroxide were as shown in Table 2. The maleic acid polymer salts for comparison (1) ~ (3) obtained were analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Examples for comparison 4 ~ 14

The procedure of example 9 was repeated to obtain the maleic acid copolymer salts for comparison (4) ~ (14) except that the other water-soluble unsaturated monomers (B) as shown in Table 2 were used in the amounts described in Table 2, the kind and amount for use of the polyvalent metal ion, and the amounts for use of the 48 % aqueous sodium hydroxide solution and 60 % hydrogen peroxide were as shown in Table 2. The maleic acid copolymer salts for comparison (4) ~ (14) were analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Example for comparison 15

In an apparatus similar to that used in the example 1 were placed 196 parts of maleic anhydride, 131 parts of monochlorobenzene, and 65.4 parts of xylene and the mixture obtained was warmed up to 140 °C. To this mixture a solution for dropping 1 composed of 65.4 parts of ditertiary-butyl peroxide, 41 parts of xylene, and 65.4 parts of monochlorobenzene, and another solution for dropping 2 composed of 26 parts of acrylic acid were added dropwise during 3 hours and then, the reaction was completed by treating under reflux for 3 hours. After the solvent was distilled off, a hydrolysis reaction was carried out with addition of 197 parts of pure water, whereby the maleic acid copolymer for comparison (15) was obtained. This maleic acid copolymer for comparison (15) was analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Example for comparison 16

In a vessel for polymerization same to that used in the example 1 were placed 196 parts of maleic anhydride and 300 parts of water (232 parts as maleic acid) and the mixture obtained was warmed up to 60 °C with stirring. The warming was stopped, and 138 parts of a 30 % aqueous sodium hydroxide solution and then 140 parts of isopropanol were added. Then, temperature of the reaction mixture was raised to the refluxing temperature and, after 0.25 parts of a 4.98 % aqueous solution of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (1 % as  $\text{Fe}^{2+}$ ) was added, 40 parts of a 60 % hydrogen peroxide were added dropwise during 6 hours. After the addition finished, further warming was carried out for 2 hours, whereby the maleic acid copolymer salt for comparison (16) was obtained, which was analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Example for comparison 17

In a vessel for polymerization same as used in the example 1 were placed 12.9 parts of 1-allyloxy-2,3-dihydroxypropane (glycerol monoallyl ether), 116 parts of maleic acid, 166.6 parts of a 48 % aqueous sodium hydroxide solution, and 157.4 parts of water and the aqueous solution thus-formed was warmed up to the boiling point. To this solution, 100 parts of a 10 % aqueous ammonium persulfate solution were added dropwise from a dropping funnel during 2 hours and, during the addition, the temperature of polymerization was always controlled at the boiling point of this reaction system. Next, the polymerization was completed by maintaining the system at the temperature for 30 minutes, whereby the maleic acid copolymer salt for comparison (17) was obtained, which was analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Example for comparison 18

The procedure of example 1 was repeated to obtain the maleic acid polymer for comparison (18) except that the 48 % aqueous sodium hydroxide solution was not used at all. This maleic acid polymer for comparison (18) was analyzed as carried out in the example 1, and the results obtained are shown in Table

2.

## Example for comparison 19

5 The maleic acid polymer salt for comparison (19) was obtained by that the maleic acid polymer for comparison (18) obtained from the example for comparison 18 was neutralized with 66.7 parts of a 48 % aqueous sodium hydroxide solution. This maleic acid polymer salt for comparison (19) was analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## 10 Example for comparison 20

The procedure of example 9 was repeated to obtain the maleic acid copolymer salt for comparison (20) except that the other water-soluble unsaturated monomer (B) as shown in Table 2 was used in the amount described in Table 2 and the kind and amount for use of the polyvalent metal ion and the amounts for use  
15 of the 48 % aqueous sodium hydroxide solution and the 60 % hydrogen peroxide were as shown in Table 2. The maleic acid copolymer salt for comparison (20) was analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

## Examples for comparison 21 and 22

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In a vessel for polymerization same as used in the example 1 were placed 232 parts of maleic acid, 200 parts of water, 0.0412 parts of ammonium ferric sulfate • 12 hydrate (as  $\text{Fe}^{3+}$ , 20 ppm against the weight of a monomer component), and 66.7 parts of a 48 % aqueous sodium hydroxide solution (20 mole % against the whole acid group of a monomer component). Then, the procedure of example 9 was repeated to obtain  
25 the maleic acid copolymer salts for comparison (21) and (22) except that the other water-soluble unsaturated monomers (B) as shown in Table 2 were used in the amounts described in Table 2. The maleic acid copolymer salts for comparison (21) and (22) were analyzed as carried out in the example 1, and the results obtained are shown in Table 2.

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Table 1 (part 1 of 3)

Example	maleic acid (co-)polymer salt	(polyvalent) metal ion ( ppm against weight of monomer component )	other water-soluble unsaturated monomer (B)	weight ratio between maleic acid and (B)	alkaline substance (mole % against whole acid group of monomer component)	hydrogen peroxide (g against 1 mole of monomer component)	amount of residual monomer (%)	biodegradation percentage (%)	molecular weight
1	(1)	VO <sup>2+</sup> (20)	—	100/0	20 (sodium hydroxide)	34	0.3	34	980
2	(2)	VO <sup>2+</sup> (20)	—	100/0	35 (sodium hydroxide)	34	0.6	27	1200
3	(3)	Fe <sup>3+</sup> (20)	—	100/0	20 (sodium hydroxide)	15	3	20	1500
4	(4)	Fe <sup>3+</sup> (20)	—	100/0	20 (sodium hydroxide)	100	0.3	37	550
5	(5)	Fe <sup>3+</sup> (2)	—	100/0	20 (sodium hydroxide)	34	3	25	980
6	(6)	Fe <sup>3+</sup> (300)	—	100/0	20 (sodium hydroxide)	34	1	25	1800
7	(7)	Fe <sup>2+</sup> (20)	—	100/0	20 (sodium hydroxide)	34	0.5	31	1010
8	(8)	Cu <sup>2+</sup> (20)	—	100/0	5 (sodium carbonate)	34	5	26	720
9	(9)	Fe <sup>3+</sup> (20)	isoprenol	80/20	20 (sodium hydroxide)	34	0.2	32	2500
10	(10)	Fe <sup>2+</sup> (20)	isoprenol	80/20	40 (sodium hydroxide)	34	0.5	28	3600
11	(11)	Fe <sup>2+</sup> (20)	isoprenol	80/20	20 (sodium hydroxide)	15	1	19	3700
12	(12)	VO <sup>2+</sup> (2)	isoprenol	80/20	20 (sodium hydroxide)	34	0.9	22	3000

Table 1 (part 2 of 3)

Example	maleic acid (co-)polymer salt	(polyvalent) metal ion (ppm against weight of monomer component)	other water-soluble unsaturated monomer (B)	weight ratio between maleic acid and (B)	alkaline substance (mole % against whole acid group of monomer component)	hydrogen peroxide (g against 1 mole of monomer component)	amount of residual monomer (%)	biodegradation percentage (%)	molecular weight
13	(13)	Fe <sup>2+</sup> (20)	isoprenol	80/20	20 (sodium hydroxide)	34	0.7	25	3100
14	(14)	Fe <sup>3+</sup> (300)	isoprenol	80/20	20 (sodium hydroxide)	34	3	31	4100
15	(15)	Cu <sup>2+</sup> (20)	isoprenol	80/20	20 (sodium hydroxide)	34	3	29	2600
16	(16)	Fe <sup>2+</sup> (20)	acrylic acid	80/20	20 (sodium hydroxide)	34	0.2	26	3200
17	(17)	Fe <sup>2+</sup> (20)	acrylic acid	75/25	20 (sodium hydroxide)	20	1	20	5500
18	(18)	Fe <sup>2+</sup> (20)	isoprenol 5 EO addition compound	80/20	20 (sodium hydroxide)	34	0.4	30	2400
19	(19)	Fe <sup>2+</sup> (20)	3-allyloxy-2-hydroxy propanesulfonic acid	80/20	20 (sodium hydroxide)	34	0.3	29	2800
20	(20)	Fe <sup>2+</sup> (20)	glycerol monoallyl ether	80/20	20 (sodium hydroxide)	34	0.5	30	2700
21	(21)	VO <sup>2+</sup> (20)	monoethyl maleate	80/20	20 (sodium hydroxide)	34	0.4	31	1400
22	(22)	VO <sup>2+</sup> (20)	glycerol monoallyl ether EO 5 moles addition compound	80/20	20 (sodium hydroxide)	34	0.4	29	2500
23	(23)	VO <sup>2+</sup> (20)	allyl alcohol EO 5 moles addition compound	80/20	20 (sodium hydroxide)	34	0.3	28	2700
24	(24)	VO <sup>2+</sup> (20)	2-acrylamido-2-methylpropane-sulfonic acid	80/20	20 (sodium hydroxide)	34	0.3	26	2900

Table 1 (part 3 of 3)

Example	maleic acid (co-)polymer salt	(polyvalent) metal ion ( ppm against weight of monomer component )	other water-soluble unsaturated monomer (B)	weight ratio between maleic acid and (B)	alkaline substance (mole % against whole acid group of monomer component)	hydrogen peroxide (g against 1 mole of monomer component)	amount of residual monomer (%)	biodegradation percentage (%)	molecular weight
25	(25)	VO <sup>3+</sup> (20)	methacrylic acid	75/25	20 (sodium hydroxide)	20	3	20	4200
26	(26)	Fe <sup>3+</sup> (20)	fumaric acid monosodium salt	80/20	20 (sodium carbonate)	34	2	30	1500
27	(27)	Fe <sup>3+</sup> (20)	itaconic acid	80/20	20 (sodium carbonate)	34	2	29	1600
28	(28)	Fe <sup>3+</sup> (20)	polyethyleneglycol monoisoprenol ether	80/20	20 (sodium carbonate)	34	2	31	3000
29	(29)	Fe <sup>3+</sup> (20)	—	100/0	20 (sodium hydroxide)	34	1	36	2000
30	(30)	Fe <sup>3+</sup> (20)	2-acrylamido-2- methylpropane- sulfonic acid	80/20	20 (sodium hydroxide)	34	0.8	28	2900
31	(31)	Fe <sup>3+</sup> (20)	acrylic acid	80/20	20 (sodium hydroxide)	34	0.3	26	3300

Table 2 (part 1 of 2)

Example for comparison	maleic acid (co-)polymer (salt) for comparison	(polyvalent) metal ion (ppm against weight of monomer component)	other water-soluble unsaturated monomer (B)	weight ratio between maleic acid and (B)	sodium hydroxide (mole % against whole acid group of monomer component)	hydrogen peroxide (g against 1 mole of monomer component)	amount of residual monomer (%)	biodegradation percentage (%)	molecular weight
1	(1)	VO <sup>2+</sup> (20)	—	100/0	50	34	2	3	2100
2	(2)	VO <sup>2+</sup> (20)	—	100/0	20	10	19	8	2200
3	(3)	absence	—	100/0	20	34	45	8	1050
4	(4)	Fe <sup>3+</sup> (20)	isoprenol	80/20	50	34	2	2	2800
5	(5)	Fe <sup>3+</sup> (20)	isoprenol	80/20	20	10	16	8	2600
6	(6)	absence	isoprenol	80/20	20	34	35	7	2400
7	(7)	Mn <sup>2+</sup> (20)	isoprenol	80/20	20	34	29	8	2500
8	(8)	Co <sup>2+</sup> (20)	isoprenol	80/20	20	34	30	7	2700
9	(9)	Mg <sup>2+</sup> (20)	isoprenol	80/20	20	34	27	6	2700
10	(10)	Ni <sup>2+</sup> (20)	isoprenol	80/20	20	34	28	8	2500
11	(11)	Zn <sup>2+</sup> (20)	isoprenol	80/20	20	34	31	7	2600
12	(12)	Fe <sup>3+</sup> (20)	2-acrylamido-2-methylpropane-sulfonic acid	50/50	20	34	5	8	5500



Table 2 (part 2 of 2)

Example for comparison	maleic acid (co-)polymer (salt) for comparison	(polyvalent) metal ion (ppm against weight of monomer component)	other water-soluble unsaturated monomer (B)	weight ratio between maleic acid and (B)	sodium hydroxide (mole % against whole acid group of monomer component)	hydrogen peroxide (g against 1 mole of monomer component)	amount of residual monomer (%)	biodegradation percentage (%)	molecular weight
13	(13)	Fe <sup>2+</sup> (20)	acrylic acid	50/50	20	34	3	8	5800
14	(14)	Fe <sup>2+</sup> (2000)	acrylic acid	80/20	20	34	7	8	5200
15	(15)	absence	acrylic acid	90/10	0	di-t-butyl peroxide (27.7)	20	3	1800
16	(16)	Fe <sup>2+</sup> (9.7)	acrylic acid	90/10	23.7	hydrogen peroxide (10.2)	25	3	1000
17	(17)	absence	glycerol monoallyl ether	90/10	100	ammonium persulfate (9.1)	12	3	1800
18	(18)	VO <sup>2+</sup> (20)	—	100/0	0	hydrogen peroxide (34)	0.3	14	1200
19	(19)	VO <sup>2+</sup> (20)	—	100/0	20 (added after polymerization)	34	0.3	15	1200
20	(20)	Fe <sup>2+</sup> (20)	acrylic acid	40/60	50	2.19	0.3	1	6000
21	(21)	Fe <sup>2+</sup> (20)	acrylic acid	50/50	20	34	6	9	2800
22	(22)	Fe <sup>2+</sup> (20)	2-acrylamido-2-methylpropane-sulfonic acid	50/50	20	34	8	9	2500

As seen in Tables 1 and 2, the maleic acid (co-) polymer salt relating to the examples, compared with the maleic acid (co-)polymer (salt) relating to the example for comparison, is less in amount of the residual monomer and superior in biodegradability. Also, when the results in Tables 1 and 2 are examined, comparing in detail, from a standpoint of difference in the reaction conditions between the examples and the examples for comparison, the undermentioned ① ~ ⑤ are seen.

① With increasing the content of maleic acid, the biodegradability increases (from comparison between the examples 29 and 30 and the example for comparison 12, and between the examples 29 and 31 and the example for comparison 13).

② If the amount of the polyvalent metal ion is large or small, the biodegradability lowers (from comparison between the examples 5, 6, and 29 and the example for comparison 3, between the examples 9 and 14 and the example for comparison 6, and between the example 16 and the example for comparison 14).

③ When a metal ion other than the ion containing vanadium atom, iron ion, and copper ion is used, the amount of the residual monomer increases and the biodegradability lowers (from comparison between the examples 9 and 15 and the examples for comparison 7 ~ 11).

④ If the neutralization extent for the whole acid group in the monomer component is 0 mole % or exceeds 45 mole %, the biodegradability lowers (from comparison between the examples 1 and 2 and the examples for comparison 1, 18, and 19, and between the examples 9 and 10 and the example for comparison 4).

⑤ If the amount of hydrogen peroxide is small, the biodegradability lowers (from comparisons between the examples 3, 4, and 29 and the example for comparison 2, and between the examples 9 and 11 and the example for comparison 5).

#### Examples 32 ~ 62

To evaluate as a scale inhibitor the properties of maleic acid (co-)polymer salts obtained from the examples 1 ~ 31, the undermentioned examinations were carried out. With 170 g of water placed in a glass bottle of 225 ml volume, 10 g of a 1.56 % aqueous calcium chloride 2-hydrate solution and 3 g of a 0.02 % aqueous solution of the maleic acid (co-)polymer salts (1)~ (31) (3 ppm against an over saturated aqueous solution obtained) were mixed and, with further additions of 10 g of a 3 % aqueous sodium hydrogencarbonate solution and 7 g of water, the total amount was adjusted to 200 g. The over saturated aqueous solution thus-obtained containing 530 ppm of sodium carbonate was tightly stoppered and treated with heating at 70 °C for 3 hours. Then, after cooling the precipitate is taken off with filtration using a membrane filter of 0.1 μ and the filtrate was analyzed.

According to the undermentioned chelate-titrating method, which is in true due to Japanese Industrial Standard; JIS KO101, the calcium concentration in the filtrate was determined.

In a beaker was placed a proper amount of a filtrate (which contained 5 mg or less as Ca) and the volume was adjusted to about 50 ml with addition of water. To this was added 4 ml of a 500 g/l aqueous potassium hydroxide solution and the solution obtained was well mixed and stood for 5 minutes, to which 0.5 ml of a 100 g/l aqueous potassium cyanide solution and 0.5 ml of a 100 g/l aqueous hydroxyl ammonium chloride (hydroxylamine hydrochloride) solution were added. Well mixing of the solution obtained gave a sample for titrating.

To a sample for titrating thus-obtained were added 5 ~ 6 drops of an aqueous solution (a NANA solution) containing 5 g/l of both 2-hydroxy-1-(2'-hydroxy-4'-sulfo-1'-naphthalenylazo)-3-naphthalenecarboxylic acid and hydroxylammonium chloride, and the solution obtained was titrated until the color becomes from reddish violet to blue with a 1 / 100 mole/l aqueous disodium ethylenediaminetetraacetate solution (a EDTA solution in which 1 ml corresponds to 0.4 mg of calcium). Besides, the EDTA solution used for titration was prepared by that disodium ethylenediaminetetraacetate 2-hydrate was dried at 80 °C for 5 hours and stood for cooling in a dessicator, then 3.722 g of it was placed in a 1 l flask and dissolved into water which was added up to a mark line of the flask.

With the following equation, the calcium concentration (mgCa/l) in the filtrate was calculated.

$$C = a \times \frac{1000}{V} \times 0.4$$

Here,

- C : calcium concentration (mgCa/l)
- a : amount of a EDTA solution required for titration (ml)
- V : amount of a filtrate used for titration (ml)
- 0.4 : amount of calcium which corresponds to 1 ml of the EDTA solution (mg)

According to the following equation, the scale inhibition percentage % for calcium carbonate was determined. The results obtained are shown in Table 3.

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$$\text{Scale inhibition percentage ( \% )} = \frac{C - B}{A - B} \times 100$$

10 A : calcium concentration dissolving in a solution before examination

B : calcium concentration in a filtrate without addition of a scale inhibitor

C : calcium concentration in a filtrate after examination Examples for comparison 23 ~ 44

In the same way as carried out for the examples 32 ~ 62, the properties as a scale inhibitor of the maleic acid (co-)polymers (salts) for comparison (1) ~ (22) obtained from the examples for comparison 1 ~ 22 were evaluated. The results obtained are shown in Table 4.

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Table 3 ( part 1 of 2 )

Example	maleic acid (co-)polymer salt used	scale inhibitor percentage for calcium carbonate (%)
3 2	maleic acid polymer salt (1)	8 8
3 3	maleic acid polymer salt (2)	8 2
3 4	maleic acid polymer salt (3)	7 7
3 5	maleic acid polymer salt (4)	8 7
3 6	maleic acid polymer salt (5)	8 0
3 7	maleic acid polymer salt (6)	8 0
3 8	maleic acid polymer salt (7)	8 5
3 9	maleic acid polymer salt (8)	8 2
4 0	maleic acid copolymer salt (9)	8 9
4 1	maleic acid copolymer salt (10)	8 8
4 2	maleic acid copolymer salt (11)	7 7
4 3	maleic acid copolymer salt (12)	8 0
4 4	maleic acid copolymer salt (13)	8 6
4 5	maleic acid copolymer salt (14)	8 0
4 6	maleic acid copolymer salt (15)	8 0

Table 3 ( part 2 of 2 )

Example	maleic acid (co-)polymer salt used	scale inhibitor percentage for calcium carbonate (%)
4 7	maleic acid copolymer salt (16)	8 7
4 8	maleic acid copolymer salt (17)	8 2
4 9	maleic acid copolymer salt (18)	8 8
5 0	maleic acid copolymer salt (19)	8 6
5 1	maleic acid copolymer salt (20)	8 5
5 2	maleic acid copolymer salt (21)	7 4
5 3	maleic acid copolymer salt (22)	8 6
5 4	maleic acid copolymer salt (23)	7 3
5 5	maleic acid copolymer salt (24)	7 2
5 6	maleic acid copolymer salt (25)	8 4
5 7	maleic acid copolymer salt (26)	7 5
5 8	maleic acid copolymer salt (27)	7 3
5 9	maleic acid copolymer salt (28)	7 3
6 0	maleic acid polymer salt (29)	8 5
6 1	maleic acid copolymer salt (30)	8 0
6 2	maleic acid copolymer salt (31)	8 1

Table 4

Example for comparison	maleic acid (co-)polymer (salt) used	scale inhibitor percentage for calcium carbonate (%)
23	maleic acid polymer salt for comparison (1)	54
24	maleic acid polymer salt for comparison (2)	63
25	maleic acid polymer salt for comparison (3)	48
26	maleic acid copolymer salt for comparison (4)	52
27	maleic acid copolymer salt for comparison (5)	65
28	maleic acid copolymer salt for comparison (6)	51
29	maleic acid copolymer salt for comparison (7)	53
30	maleic acid copolymer salt for comparison (8)	52
31	maleic acid copolymer salt for comparison (9)	53
32	maleic acid copolymer salt for comparison (10)	55
33	maleic acid copolymer salt for comparison (11)	51
34	maleic acid copolymer salt for comparison (12)	48
35	maleic acid copolymer salt for comparison (13)	49
36	maleic acid copolymer salt for comparison (14)	45
37	maleic acid copolymer for comparison (15)	53
38	maleic acid copolymer salt for comparison (16)	58
39	maleic acid copolymer salt for comparison (17)	70
40	maleic acid polymer for comparison (18)	83
41	maleic acid polymer salt for comparison (19)	81
42	maleic acid copolymer salt for comparison (20)	51
43	maleic acid copolymer salt for comparison (21)	49
44	maleic acid copolymer salt for comparison (22)	49

## Examples 63 ~ 93

To evaluate the properties as a cleaner builder of the maleic acid (co-)polymer salts (1) ~ (31) obtained from the examples 1 ~ 31, the undermentioned examinations were carried out. Into 50 ml of a  $10^{-3}$  mol/l aqueous calcium chloride solution were added 10 mg (calculated on a basis of the solid portion) of the maleic acid (co-)polymer salts (1)~ (31), obtained from the examples 1 ~ 31, and using an ion analyzer (MODEL 701) made from Orion Co., Ltd. and a calcium ion electrode, the amounts of calcium ion blocked by the maleic acid (co-)polymer salts (1) ~ (31) were determined and the chelating ability of each maleic acid (co-)polymer salts were measured with the following equation, and the results obtained are shown in Table 5.

$$\text{chelating ability} = \frac{\text{mg of calcium blocked ( converted into } \text{CaCO}_3 \text{ )}}{\text{g of maleic acid ( co-)polymer salt ( converted into the solid portion )}}$$

Examples for comparison 45 ~ 66

In the same way as carried out for the examples 63 ~ 93, maleic acid (co-)polymers (salts) for comparison (1) ~ (22) obtained from the examples for comparison 1 ~ 22 were evaluated in the properties when used as a detergent builder, and the results obtained are shown in Table 6.

T a b l e 5 ( part 1 of 2 )

Example	maleic acid (co-)polymer salt used	chelating ability ( mgCaCO <sub>3</sub> /g )
6 3	maleic acid polymer salt (1)	2 8 0
6 4	maleic acid polymer salt (2)	3 3 0
6 5	maleic acid polymer salt (3)	2 5 0
6 6	maleic acid polymer salt (4)	2 7 5
6 7	maleic acid polymer salt (5)	2 4 5
6 8	maleic acid polymer salt (6)	2 5 5
6 9	maleic acid polymer salt (7)	2 6 0
7 0	maleic acid polymer salt (8)	2 5 0
7 1	maleic acid copolymer salt (9)	2 4 0
7 2	maleic acid copolymer salt (10)	3 0 5
7 3	maleic acid copolymer salt (11)	2 3 5
7 4	maleic acid copolymer salt (12)	2 4 0
7 5	maleic acid copolymer salt (13)	2 4 0
7 6	maleic acid copolymer salt (14)	2 5 0
7 7	maleic acid copolymer salt (15)	2 4 0

Table 5 ( part 2 of 2 )

Example	maleic acid (co-)polymer salt used	chelating ability ( mgCaCO <sub>3</sub> /g )
7 8	maleic acid copolymer salt (16)	2 5 5
7 9	maleic acid copolymer salt (17)	2 6 5
8 0	maleic acid copolymer salt (18)	2 4 0
8 1	maleic acid copolymer salt (19)	2 5 0
8 2	maleic acid copolymer salt (20)	2 5 0
8 3	maleic acid copolymer salt (21)	2 1 0
8 4	maleic acid copolymer salt (22)	2 5 0
8 5	maleic acid copolymer salt (23)	2 1 5
8 6	maleic acid copolymer salt (24)	2 0 5
8 7	maleic acid copolymer salt (25)	2 6 5
8 8	maleic acid copolymer salt (26)	2 1 5
8 9	maleic acid copolymer salt (27)	2 1 0
9 0	maleic acid copolymer salt (28)	2 2 0
9 1	maleic acid polymer salt (29)	2 8 2
9 2	maleic acid copolymer salt (30)	2 6 0
9 3	maleic acid copolymer salt (31)	2 6 5



Table 6

Example for comparison	maleic acid (co-)polymer (salt) used	chelating ability [mgCaCO <sub>3</sub> /g]
45	maleic acid polymer salt for comparison (1)	180
46	maleic acid polymer salt for comparison (2)	177
47	maleic acid polymer salt for comparison (3)	110
48	maleic acid copolymer salt for comparison (4)	186
49	maleic acid copolymer salt for comparison (5)	170
50	maleic acid copolymer salt for comparison (6)	105
51	maleic acid copolymer salt for comparison (7)	183
52	maleic acid copolymer salt for comparison (8)	180
53	maleic acid copolymer salt for comparison (9)	118
54	maleic acid copolymer salt for comparison (10)	120
55	maleic acid copolymer salt for comparison (11)	123
56	maleic acid copolymer salt for comparison (12)	165
57	maleic acid copolymer salt for comparison (13)	168
58	maleic acid copolymer salt for comparison (14)	160
59	maleic acid copolymer for comparison (15)	135
60	maleic acid copolymer salt for comparison (16)	164
61	maleic acid copolymer salt for comparison (17)	185
62	maleic acid polymer for comparison (18)	248
63	maleic acid polymer salt for comparison (19)	243
64	maleic acid copolymer salt for comparison (20)	170
65	maleic acid copolymer salt for comparison (21)	155
66	maleic acid copolymer salt for comparison (22)	158

As seen in Tables 3 ~ 6, it is understood that a superior scale inhibitor and a detergent builder led from the maleic acid (co-)polymer salt in the examples are much superior to those led from the maleic acid (co-)polymer (salt) in the examples for comparison.

#### Claims

1. A process for producing a maleic acid (co-)polymer salt improved in biodegradability, said process comprising polymerizing a monomer component composed of from 75 to 100 weight % of maleic acid (A) and of from 0 to 25 weight % of another water-soluble unsaturated monomer (B) (wherein the total amount of (A) and (B) is 100 weight %) with water as solvent in the presence of:
  - a) 12 to 150g (per 1 mole of the monomer component) hydrogen peroxide as a polymerization catalyst;
  - b) 0.3 to 500ppm (per weight of the monomer component) of at least one kind of polyvalent metal ion selected from an ion containing a vanadium atom, an iron ion, and a copper ion; and
  - c) an alkaline substance in sufficient quantity to neutralise 45 mole % or less (but excluding 0 mole %) of the whole acid group of the monomer component.
2. A process as claimed in Claim 1 wherein the monomer component is composed of from 80 to 100 weight % of maleic acid (A) and of from 20 to 0 weight % of another water-soluble unsaturated

monomer (B) (wherein the total amount of (A) and (B) is 100 weight %).

3. A process as claimed in either of Claims 1 and 2 wherein of from 20 to 70g (per 1 mole of the monomer component) hydrogen peroxide is present.
- 5 4. A process as claimed in any one of Claims 1 to 3 wherein the amount of alkaline substance present during polymerization is of from 5 to 40 mole % per whole acid group of the monomer component.
- 10 5. A process as claimed in any one of Claims 1 to 4 wherein of from 1 to 50ppm (per weight of the monomer component) of a polyvalent metal ion is present.
6. A process as claimed in any one of Claims 1 to 5 wherein the polyvalent metal ion  $\text{VO}^{2+}$  is present.
7. A process as claimed in any one of Claims 1 to 6 wherein the polyvalent metal ion  $\text{Fe}^{3+}$  is present.
- 15 8. A process as claimed in any one of Claims 1 to 7 wherein the polyvalent metal ion  $\text{Cu}^{2+}$  is present.
9. A maleic acid (co-)polymer salt obtainable by the process as claimed in any one of Claims 1 to 8.
- 20 10. Use of a maleic acid (co-)polymer salt as claimed in Claim 9 as a detergent builder.
11. Use of a maleic acid (co-)polymer salt as claimed in Claim 9 as a scale inhibitor.

#### Patentansprüche

- 25 1. Verfahren zur Herstellung eines Maleinsäure-(Co-)Polymersalzes mit einem verbesserten biologischen Abbauvermögen, wobei das Verfahren aus einem Polymerisieren einer monomeren Komponente besteht, die aus 75 bis 100 Gew.-% Maleinsäure (A) und aus 0 bis 25 Gew.-% eines anderen wasserlöslichen ungesättigten Monomers (B) besteht (wobei die Gesamtmenge von (A) und (B) 100 Gew.-% beträgt), zusammen mit Wasser als Lösungsmittel in der Gegenwart von:
  - a) 12 bis 150g (pro 1 Mol der monomeren Komponente) Wasserstoffperoxid als ein Polymerisationskatalysator;
  - b) 0.3 bis 500 ppm (pro Gewicht der monomeren Komponente) wenigstens einer Art eines polyvalenten Metallions, ausgewählt von einem Ion, welches ein Vanadiumatom, ein Eisenion und ein Kupferion enthält; und
  - 35 c) einer alkalischen Substanz in einer genügenden Menge, um 45 Mol-% oder weniger (aber unter Ausschluß von 0 Mol-%) der gesamten Säuregruppe der monomeren Komponente zu neutralisieren.
- 40 2. Verfahren nach Anspruch 1, bei welchem die monomere Komponente aus 80 bis 100 Gew.-% Maleinsäure (A) und aus 20 bis 0 Gew.-% eines anderen wasserlöslichen ungesättigten Monomers (B) zusammengesetzt ist (wobei die Gesamtmenge von (A) und (B) 100 Gew.-% beträgt).
3. Verfahren nach einem der Ansprüche 1 und 2, bei welchem von 20 bis 70g (je 1 Mol der monomeren Komponente) Wasserstoffperoxid vorhanden ist.
- 45 4. Verfahren nach einem der Ansprüche 1 bis 3, bei welchem die Menge der während der Polymerisation vorhandenen alkalischen Substanz von 5 bis 40 Mol-% pro gesamter Säuregruppe der monomeren Komponente beträgt.
- 50 5. Verfahren nach einem der Ansprüche 1 bis 4, bei welchem von 1 bis 50 ppm (pro Gewicht der monomeren Komponente) eines polyvalenten Metallions vorhanden ist.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei welchem das polyvalente Metallion  $\text{VO}^{2+}$  vorhanden ist.
- 55 7. Verfahren nach einem der Ansprüche 1 bis 6, bei welchem das polyvalente Metallion  $\text{Fe}^{3+}$  vorhanden ist.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem das polyvalente Metallion  $\text{Cu}^{2+}$  vorhanden ist.

9. Maleinsäure-(Co-)Polymersalz, das durch das Verfahren nach einem der Ansprüche 1 bis 8 zu erhalten ist.

10. Verwendung eines Maleinsäure-(Co-)Polymersalzes nach Anspruch 9 als ein Detergenzbildner.

11. Verwendung eines Maleinsäure-(Co-)Polymersalzes nach Anspruch 9 als ein Schuppen-Inhibitor.

## Revendications

1. Procédé pour la préparation d'un (co)polymère d'un sel d'acide maléique avec une biodégradabilité modifiée, ledit procédé comprenant la polymérisation d'un constituant monomère composé à 75 - 100 % en poids d'acide maléique (A) et de 0 - 25 % en poids d'un autre monomère insaturé hydrosoluble (B), (la quantité totale (A) + (B) étant égale à 100 % en poids), avec de l'eau utilisée comme solvant et en présence de :

a) 12 à 150 g (pour 1 mole du constituant monomère) de peroxyde d'hydrogène comme catalyseur de polymérisation,

b) 0,3 à 500 ppm (en poids du constituant monomère) d'au moins un type d'ion métallique polyvalent choisi parmi un ion contenant un atome de vanadium, un ion de fer et un ion de cuivre,

c) une substance alcaline en quantité suffisante pour neutraliser 45 % en moles ou moins (excepté 0 % en moles) de la fonction acide totale du constituant monomère.

2. Procédé selon la revendication 1, caractérisé en ce que le constituant monomère est composé à 80 - 100 % en poids d'acide maléique (A) et de 20 - 0 % en poids d'un autre monomère insaturé hydrosoluble (B), (la quantité totale (A) + (B) étant égale à 100 % en poids).

3. Procédé selon les revendications 1 et 2, caractérisé en ce que le peroxyde d'hydrogène est présent à raison de 20 - 70 g (pour 1 mole de constituant monomère).

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la quantité de substance alcaline présente pendant la polymérisation s'élève à 5 - 40% en moles par fonction acide totale du constituant monomère.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce qu'un ion métallique polyvalent est présent à raison de 1 - 50 ppm (en poids du constituant monomère).

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que l'ion métallique polyvalent  $\text{VO}^{2+}$  est présent.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que l'ion métallique polyvalent  $\text{Fe}^{3+}$  est présent.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que l'ion métallique polyvalent  $\text{Cu}^{2+}$  est présent.

9. (Co)polymère d'un sel d'acide maléique réalisable conformément au procédé selon l'une quelconque des revendications 1 à 8.

10. Emploi d'un (co)polymère d'un sel d'acide maléique selon la revendication 9 en tant qu'adjuvant détergent.

11. Emploi d'un (co)polymère d'un sel d'acide maléique selon la revendication 9 en tant qu'inhibiteur de dépôts écailleux.

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